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In the original paper using the thin film wrinkling technique, results were presented for the rubbery plateau modulus and viscosity of a polystyrene (PS) material having a molecular mass of approximately  $600 \text{ kg mol}^{-1}$ . The wrinkling technique itself, for the elastic case, is fully described in a number of previous publications. The comments are concerned with the viscoelastic analysis and the data presented for the polystyrene relative to that in the macroscopic state. In particular, we show that there is an error of several orders of magnitude in the reported macroscopic viscosity for the PS and these were, seemingly, consistent with the thin film results. This suggests that the method is not refined enough to provide viscoelastic data in the long time regime of polymers. We also show that the values of the rubbery modulus determined for the thin polymer film are highly sensitive to the assumptions made for the Poisson's ratio of the polymer in the (nearly incompressible) rubbery state. The viscosity estimates are also sensitive to the assumed value of Poisson's ratio, but not sufficiently to explain the orders of magnitude differences with literature reports. Because of issues with the constrained thin film analysis, we examine here an analysis of the data using a conventional analytical solution for a thick compliant layer, i.e. where the material is not confined, and again find that the results for the PS film are not consistent with measured bulk properties. This suggests that these thin film wrinkling experiments may be in a region where the confinement is not well defined and/or that further refinement to the reported viscoelastic model is required to fully capture the viscoelastic properties of confined polymer films.

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Comment on "Viscoelastic properties of confined     ...

Block 13: Supplementary Note

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# Comment on “Viscoelastic properties of confined polymer films measured *via* thermal wrinkling” by E. P. Chan, K. A. Page, S. H. Im, D. L. Patton, R. Huang, and C. M. Stafford, *Soft Matter*, 2009, 5, 4638–4641

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Recently Chan *et al.* published a paper<sup>1</sup> describing a method that used thermal wrinkling of a thin polymer film on which is adhered a thin metal film to extract the viscoelastic properties of the polymer. Results were presented for the rubbery plateau modulus and viscosity of a polystyrene (PS) material having a molecular mass of approximately 600 kg mol<sup>−1</sup>. The wrinkling technique itself, for the elastic case, is fully described in a number of previous publications.<sup>2,3</sup> Our comments are concerned with the viscoelastic analysis and the data presented for the polystyrene relative to that in the macroscopic state. In particular, we show that there is an error of several orders of magnitude in the reported macroscopic viscosity for the PS and these were, seemingly, consistent with the thin film results. This suggests that the method is not refined enough to provide viscoelastic data in the long time regime of polymers. We also show that the values of the rubbery modulus determined for the thin polymer film are highly sensitive to the assumptions made for the Poisson’s ratio of the polymer in the (nearly incompressible) rubbery state. The viscosity estimates are also sensitive to the assumed value of Poisson’s ratio, but not sufficiently to explain the orders of magnitude differences with literature

reports. Because of issues with the constrained thin film analysis, we examine here an analysis of the data using a conventional analytical solution for a thick compliant layer, *i.e.* where the material is not confined, and again find that the results for the PS film are not consistent with measured bulk properties. This suggests that these thin film wrinkling experiments may be in a region where the confinement is not well defined and/or that further refinement to the reported viscoelastic model<sup>1</sup> is required to fully capture the viscoelastic properties of confined polymer films.

To briefly summarize the experimental approach, the system is comprised of PS supported on a silicon substrate and then capped with an aluminium film. Upon heating, the polymer/metal film undergoes wrinkling due to compressive stresses generated by thermal expansion mismatches. The wrinkle wavelength and amplitude were recorded as a function of time and temperature and were interpreted to be related to the rubbery modulus and the viscosity of the polymer film using a model of viscoelastic wrinkling under confinement.<sup>4</sup> All temperatures were above the macroscopic glass transition temperature  $T_g$  of the PS. From the data, a limiting long-time wavelength,  $d_r$ , is determined as well as an amplitude growth rate,  $S$ , found from the initial (exponential) growth in the amplitude. These data are then used to determine the elastic rubbery modulus,  $E_{i,r}$ , and the shear viscosity,  $\eta$ , respectively for the PS layer.

The rubbery modulus  $E_{i,r}$  was calculated using:

$$E_{i,r} = \frac{(1 - 2\nu_i)(1 + \nu_i)}{12(1 - \nu_i)} \left( \frac{h_i}{h_f} \right) \times \left( \frac{2\pi h_f}{d_r} \right)^4 \frac{E_f}{1 - \nu_f^2}, \quad (1)$$

where  $h_i$  and  $h_f$  are the thickness of the viscoelastic film (PS) and the stiff elastic support film (Al) respectively.  $E_f$  is the stiffness of the Al film,  $\nu_f$  the Poisson’s ratio of the Al film and  $\nu_i$  the Poisson’s ratio of the viscoelastic PS film. The Al was assumed to have a modulus of  $E_f = 7 \times 10^{10}$  N m<sup>−2</sup> and a Poisson’s ratio of  $\nu_f = 0.33$ , and the measured thickness was  $h_f = 54$  nm. The PS film was assumed to have a Poisson’s ratio of  $\nu_i = 0.495$ , and the measured thickness was  $h_i = 270$  nm. This is thick enough that one would anticipate that the PS film should exhibit macroscopic viscoelastic behavior.

Chan *et al.* report the rubbery modulus  $E_{i,r}$  (in uniaxial compression) at 125 °C to be approximately  $3.1 \times 10^5$  N m<sup>−2</sup>. This is lower than, though compares favorably to, the macroscopic value of the rubbery modulus reported by Plazek<sup>5</sup> ( $E \approx 1 \times 10^6$  N m<sup>−2</sup> – converted from the shear compliance ( $J$ ) to the uniaxial stiffness ( $E$ ) by the expression  $J = 1/3E$  for an incompressible elastic material). However, in Chan *et al.*, the Poisson’s ratio  $\nu$  assumed for the PS layer was 0.495, which gives a very unrealistic value for the bulk modulus  $K$  of the polymer above its glass transition, as is now shown. Again assuming elastic behavior, the relationship between  $K$ ,  $E$ , and  $\nu$  is

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$$K = \frac{E}{3(1-2\nu)}. \quad (2)$$

Using the value  $E = 3.1 \times 10^5 \text{ N m}^{-2}$  above and  $\nu = 0.495$  [as used in the original paper], we find that  $K = 3.1 \times 10^7 \text{ N m}^{-2}$ . This is far different from reported bulk modulus values for PS above its  $T_g$ . Meng *et al.*<sup>6</sup> report  $K = 1.38 \times 10^9 \text{ N m}^{-2}$  at 160 °C for PS having a mass average molecular mass of 221 kg mol<sup>-1</sup>, and they report data from Rehage *et al.*<sup>7</sup> and Hellwege<sup>8</sup> for PS of  $K = 1.5 \times 10^9 \text{ N m}^{-2}$  (at 155 °C) and  $1.7 \times 10^9 \text{ N m}^{-2}$  (at 162.3 °C), respectively. In addition, pressure–volume–temperature data<sup>9</sup> for PS having a mass average molecular mass of 110 kg mol<sup>-1</sup> extrapolated to zero pressure at 125 °C gives  $K = 1.49 \times 10^9 \text{ N m}^{-2}$ . These values are significantly higher than the inferred value of  $3.1 \times 10^7 \text{ N m}^{-2}$  just discussed and imply that the value of the Poisson's ratio  $\nu = 0.495$  is incorrect. This result is due to the high sensitivity of the modulus values to small changes in  $\nu$ .<sup>10,11</sup> If, on the other hand, we use the bulk modulus value of  $2 \times 10^9 \text{ N m}^{-2}$  and the value for the rubbery stiffness from the wrinkling experiments at 125 °C given above, we get the value for Poisson's ratio, from eqn (2), to be  $\nu = 0.4999$ . Moreover, eqn (1) for the wrinkling experiment shows that the term  $(1-2\nu_i)$  in the numerator leads to an asymptotic approach of the rubbery modulus  $E_{i,r}$  to zero as  $\nu_i$  approaches 0.5. Hence, in the analysis of the wrinkling experiments, the modulus is a strong function of the Poisson's ratio. For example, the moduli calculated using eqn (1) for PS at 125 °C for  $\nu_i = 0.48$  and  $\nu_i = 0.499$  differ by a factor of approximately 20. Due to this high sensitivity to the assumed Poisson's ratio, it may be that the analytical equations need to be recast in terms that do not include the Poisson's ratio.

In order to examine possible reasons for the large discrepancies in the thin film behavior, which should approach macroscopic behavior for the film thickness studied by Chan *et al.*, we consider the possibility that, under the experimental conditions, the material does not meet the confinement criteria required for application of eqn (1)–(3) and so these expressions would not be expected to describe the viscoelastic response of the

PS layer. It is not clear under what conditions [*e.g.* thickness ( $h_i/h_f$ ) and/or modulus ratio ( $E_i/E_f$ )] that a material can be considered to be under confinement, and interestingly eqn (1) does not revert to the bulk analytical solution for a polymer layer of infinite thickness. However, as a bounding limit we can apply the bulk analytical solutions to the data. The conventional analytical solution for a thick compliant layer ( $h_i \gg h_f$ ) is given as:<sup>2,4</sup>

$$E_i = \frac{1}{3}(1-\nu_i^2) \left( \frac{E_f}{1-\nu_f^2} \right) \left( \frac{d_r}{2\pi h_f} \right)^{-3}, \quad (5)$$

where the variables are as before. Using this equation to solve for the modulus of the PS layer using wrinkling data yields values ranging from  $E_i = 4.7 \times 10^7 \text{ N m}^{-2}$  to  $4.1 \times 10^7 \text{ N m}^{-2}$  over the temperature range 120 °C to 135 °C. Again comparing these data to the results of Plazek ( $E_i = 1 \times 10^6 \text{ N m}^{-2}$ ) these moduli are some 50 times stiffer than would be expected for a bulk response.

Similar to the discussion above regarding the rubbery modulus, the analysis for the viscosity from the film wrinkling experiment is also highly sensitive to the Poisson's ratio. In this case the viscosity,  $\eta_i$ , was related to the experimentally determined growth rate parameter,  $S$ , as:

$$\eta_i = - \frac{\frac{1-2\nu_i}{1-\nu_i} \left( \frac{h_i}{h_f} \right) \left( \frac{E_f}{12(1-\nu_f^2)} \left( \frac{2\pi h_f}{d} \right)^4 + \sigma \left( \frac{2\pi h_f}{d} \right)^2 \right) + \frac{E_i}{1+\nu_i}}{2S} \quad (3)$$

where the variables are as before. The  $\sigma$  term is the compressive stress in the elastic (Al) film and was estimated to be  $\approx 3 \times 10^8 \text{ N m}^{-2}$ , slightly below the yield stress of bulk aluminium. As with the modulus, the viscosity depends on the value of the Poisson's ratio that is assumed. Again for

$$\eta_i = - \left[ \frac{\frac{E_f}{24} \left( \frac{2\pi h_f}{d} \right)^3 + 12\sigma (1-\nu_f^2) \left( \frac{2\pi h_f}{d} \right) + \frac{E_i}{2(1+\nu_i)}}{S} \right] \quad (6)$$

the range of  $\nu_i = 0.48$  to  $\nu_i = 0.499$ , the viscosity changes by a factor of 20 and approaches zero as  $\nu_i$  tends to 0.5.

We plot in Fig. 1 the log of the zero-shear rate viscosity as a function of temperature reported by Chan *et al.* for

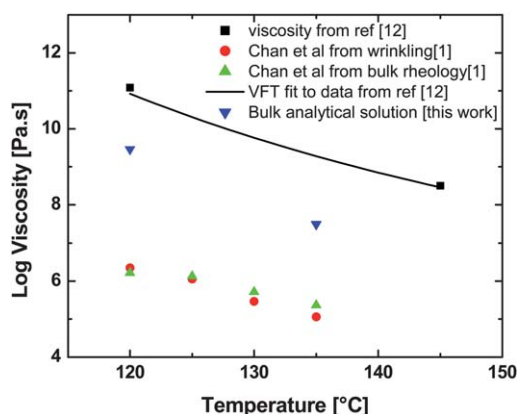
600 kg mol<sup>-1</sup> PS, obtained both for the thin film wrinkling experiments and from bulk rheological measurements. For comparison, we show previously reported results for a 592 kg mol<sup>-1</sup> PS.<sup>12</sup> It is clear that the literature data disagree with both the macroscopic and thin film data reported by Chan *et al.* by some 4 to 5 orders of magnitude. There is clearly a large discrepancy, suggesting that the viscosity obtained by wrinkling is inaccurate, likely due to the overly simplistic viscoelastic model employed in deriving the analytical expressions, and that the macroscopic measurements reported were also in error for unknown reasons. We note here that care must be exercised when measuring the viscosity of long chain polymers as the time to achieve steady state can be significant. For a simple Maxwell-type model the steady state viscosity,  $\eta$ , is related to the rubbery modulus,  $G$ , and the relaxation time,  $\tau$ , by<sup>5</sup>

$$\eta = G \cdot \tau \quad (4)$$

Taking the viscosity to be  $\approx 2 \times 10^{10} \text{ Pa s}$  and the modulus to be  $3 \times 10^5 \text{ N m}^{-2}$  gives a relaxation time of approximately 18.5 h, indicative of the minimum time required for the material to reach steady state.

Accordingly, the analysis for the shear viscosity,  $\eta_i$ , from the film wrinkling experiment needs to be replaced by the relationship for bulk response. In this case the shear viscosity of PS, assuming the polymer layer is not under confinement and is nearly incompressible becomes:

and the variables are as before. Using this bulk analytical solution yields shear viscosities ranging from  $2.9 \times 10^9 \text{ N s m}^{-2}$  to  $3.1 \times 10^7 \text{ N s m}^{-2}$  over the temperature range of 120 °C to 135 °C. These data are included in Fig. 1 and, while closer to the



**Fig. 1** Log viscosity vs. temperature from both wrinkling and bulk experiments reported in ref. 1. Also shown are viscosity data from McKenna *et al.*<sup>12</sup> and viscosity data from the unconstrained wrinkling solution (eqn (6)).

bulk data of ref. 12, are still some two orders of magnitude lower. Moreover, a plot of the viscosity as a function of temperature, at temperatures greater than the glass transition temperature, should follow a non-Arrhenius type response as indicated in Fig. 1 for the macroscopic data, though the limited temperature range studied in the wrinkling work may make it difficult to determine the exact form of the temperature dependence. We also remark that near to yield, the elastic (Al) film itself may begin to show time-dependent plasticity effects and this may suggest a more elastic material is needed for the superstrate.

As a final observation we remark that the meaning of the viscosity as introduced in the paper under discussion is unclear. The rubbery modulus is determined from the long time plateau in the wrinkle wavelength vs. time plot (*i.e.*,  $d_r$ ). The early time data may then be reasonably associated with the short time viscoelastic response of the material (PS) under the action of the compressive stress from the Al film (essentially a creep test). However, it is this same early time data that is used to determine the growth rate parameter,  $S$ , used in the calculation of the shear

viscosity. The viscosity would normally be measured from the strain rate data at times sufficiently large that the material has moved through the rubbery plateau region and is in the terminal flow region. However, this deformation history is not achieved in thermal wrinkling since a constant (and for a long time) strain rate cannot be directly applied to the system but rather is convoluted due to the fact that the applied deformation is related to both the heating and the buckling events. As was discussed in ref. 1, the shear viscosity measured from thermal wrinkling is determined from the short-time response of the polymer layer due to the thermal mismatch stress. The growth rate  $S$  gives an indication of the applied strain rate, however, the specific value of  $S$  depends on many factors including the thickness of the superstrate, the CTE values and the testing temperature.

In summary, while the thin film wrinkling technique promises to be a useful tool for probing the properties of materials at the nanoscale, further refinement of the model and analysis is required before quantitative data can be extracted. Ideally, such a model would be a general

solution that spans regimes that are bulk-like down to highly confined.

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